Capacitance property of carbon material derived from starch mixed with guanidine phosphate as electrochemical capacitor

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HIGHLIGHTS

- ► The effect of the addition of guanidine phosphate to starch before the heating process was investigated.
- ► Enhancement of the surface area is the main reason for the enhanced capacitance value.
- ► Suppression of the electrical resistance is one of the reasons for the improved capacitance.
- ► The electrical double layer capacitance per unit area did not contribute to the change in capacitance.
- ► The appearance of a pseudo capacitance is one of the reasons for the improved capacitance.

GRAPHICAL ABSTRACT
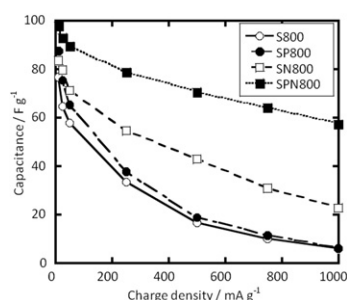
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ABSTRACT

We have already reported that the addition of guanidine phosphate increased the capacitance values as the electrode of an electrochemical capacitor for the carbon material derived from starch. If this method, that is, the addition of a compound containing hetero atoms such as N and P before the heat treatment for the carbonization is effective for improving the performance as the electrode of an electrochemical capacitor, then a high performance material can be developed by this method. Therefore, in this study, the effect of the addition of guanidine phosphate with starch is investigated in detail. The change in the surface area, which could be caused by P, is the main reason for enhancement of the capacitance value. The wettability against water is not improved by the addition of guanidine phosphate. The electrical resistance decreased by the addition of guanidine phosphate. This decrease should be one of the reasons for the improved capacitance value. The electrical double layer capacitance per surface area did not increase, whereas the change in the pseudo capacitance could be one of the reasons for the improved capacitance value.

1. Introduction

Many research studies have recently been carried out for the development of electrochemical capacitors. In order to improve the performance of the electrochemical capacitor, the studies of electrode materials were performed because the electrode is the most

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important part for the storage. Many approaches have been proposed for the improvement. Some researchers have reported that the addition of a hetero element such as N, P, etc., is effective for the improved capacitance [1–6], and the effect of the addition has been under discussion [7–9]. As for the N-containing electrodes, most of the research has involved using nitrogen-containing resins, such as melamine resin and polyacrylonitrile, as precursors [1–3]. As for the addition of P, inorganic compounds, such as phosphoric acid, have been used as the P source [4–7,10,11]. However, in most of the studies using phosphoric acid, the purpose of the addition was for activating the carbon material [10,11].

It is known that phosphoric compound acts as the flame retardant for cellulose [12]. The presumed mechanism is as follows. The phosphoric compound changed into phosphorous and phosphoric acid during the combustion process, and then these acids acted as the catalyst for dehydration reaction [12,13]. This should mean that the phosphoric compound affect the carbonization process of cellulose. Some research works reported that the nitrogen addition with phosphoric compound was effective for the change in the flame retardant property [12–18]. Although the reason for the change was proposed by Granzow [12] and Gaan et al. [13], the mechanism is under discussion. Even if the mechanism is unclear, the nitrogen added with phosphorus should affect the carbonization process of cellulose. Therefore, the chemical condition of the carbon material synthesized by the heat treatment of the polysaccharide such as cellulose could depend on the addition of phosphorous−nitrogen compounds. It is known that phosphoric acid acts as the activator for enhancing the surface area of carbon material. Some of the carbon materials containing nitrogen had high performance as the electrode of electrochemical capacitor. Moreover, it is known that some of nitrogen is retained in the char while in the absence of a phosphorous compound the nitrogen is quantitatively volatilized [12]. Therefore, the existence of both the phosphorus and the nitrogen in the sample could have positive effects on the performance as the electrode of electrochemical capacitor of the sample.

It is known that guanidine phosphate $((C(NH)(NH_2)_2)_2H_3PO_4)$ acts as a flame retardant for cellulose, which is a polysaccharide. Because starch is a polysaccharide, we can expect a similar effect of guanidine phosphate on starch. We have already reported that the addition of guanidine phosphate is effective for improvement of the capacitive performance of a carbon material derived from starch in a H_2SO_4 aqueous solution [19]. This method, that is, the addition of guanidine phosphate before the heating process, is simple, easy, safe, and inexpensive. Therefore, this method should be valuable in practical use. In this study, we investigated the performance of the samples in detail.

2. Experimental

Starch (Starch, soluble; Wako) was mixed with guanidine carbonate or guanidine phosphate. The weight ratio of guanidine phosphate to starch was from 1:20 to 1:3, that is, from 4.8 wt.% to 25.0 wt.%. The mixed powder was then added to distilled water. The amount of the added water was sufficient to cover the mixed powder. The slurry mixture was manually mixed for *ca.* 3 min. In the case of guanidine carbonate, the weight ratio of guanidine carbonate to starch was 1:20, that is, 4.8 wt.%. In the case of phosphoric acid, the mole number of P in the added phosphoric acid water solution was the same as that in the sample-added guanidine phosphate of 4.8 wt.%. The slurry was completely dried in a dryer at 80 °C (approximately 72 h). The dried powder was then heated at 800 °C for 1 h in flowing N_2 (*ca.* 50 mL min^{-1}). The heating rate was *ca.* 20 °C min^{-1}. The samples prepared only from starch, and those prepared from starch mixed with phosphoric acid,

guanidine carbonate, and guanidine phosphate are subsequently referred to as S-800, S-P800, S-N800, and S-PN800, respectively. As for the samples washed with hot water "W" is added after the abbreviation, for example, S-PN800 − >S-PN800W.

The powders were used for the TG-DTA, BET, XPS and CHN-corder measurements. For the TG-DTA measurements, the mixed powders before the heat treatment were used in order to investigate the effect of the heat treatment. The TG-DTA measurements were performed up to 1000 °C at the rate of 10 K min^{-1} in flowing N_2.

The powder prepared by the heat treatment, acetylene black, and Teflon powder were mixed in the weight ratio of 8:1:1 to form a sheet. In order to evaluate the wettability of the sheet sample, the contact angle against distilled water was measured. The sheet was cut (20 mm*8 mm*0.5 mm) and then used as the electrode for the electrochemical measurements, such as the cyclic voltammetric (CV) measurements and galvanostatic charge/discharge cycles. The CV measurements and galvanostatic charge/discharge cycles measurements were performed in a 1 M H_2SO_4 water solution, and a Pt plate was used as the counter electrode and the Ag/AgCl electrode was used as the reference electrode. A Pt plate was used as the collecting electrode. The AC impedance measurements were performed in order to estimate the electrical resistance.

3. Results and discussion

3.1. Performance as the electrode of capacitor

The CV curves of the samples are shown in Fig. 1. The CV graph for S-800 was a rectangular shape. The shapes of the CV curves deformed in the case of the samples added the additives. Moreover, the areas of the CV curves were enhanced by the addition of the additives, except for S-P800. These experimental results should mean that the addition of the additives affected the electrochemical property of starch.

The results of the charge/discharge measurements are shown in Fig. 2. It should be noticed that the capacitance values increased by the addition of the additives. The samples mixed with the nitrogen containing compounds, such as S-N800 and S-PN800, had much larger capacitance value than S-800. Especially, S-PN800 had the largest capacitance value of all the samples.
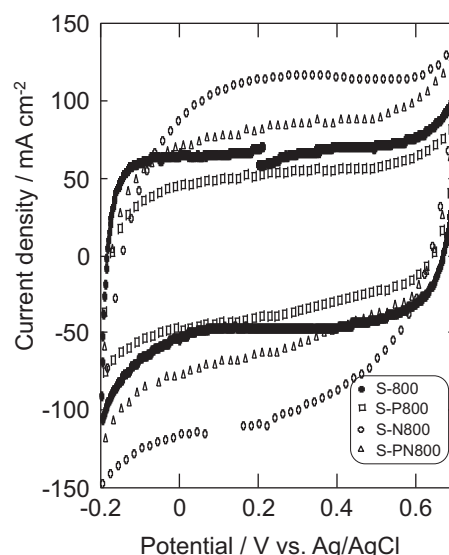
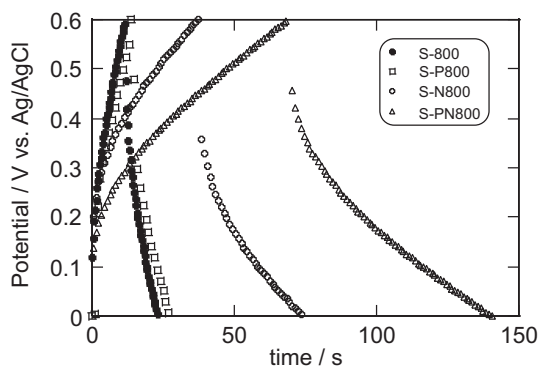

Fig. 1. CV curves of the samples. (scan rate: 1 mV s^{-1}).

Fig. 2. Charge/discharge measurements of the samples. (Current density: 500 mA g^{-1}).

The current density dependence of the capacitance values of the samples are shown in Fig. 3. These results show that the samples mixed with the additives had higher capacitance values than the sample derived from only starch, that is, S-800. Therefore, we can conclude that the blends of the additive were effective for enhancing of the capacitance values. The sample with added guanidine phosphate, which contains P and N, had the highest capacitance values in all the current density range. Therefore, we investigated the effect of guanidine phosphate in detail.

3.2. TG-DTA measurements

The experimental results of the TG-DTA measurements are shown in Fig. 4 and Fig. 5. The weight of starch rapidly decreased at *ca.* 280 °C, and about 80% of the weight was lost up to *ca.* 350 °C as shown in Fig. 4a. The starting temperatures of the weight loss decreased with the addition of guanidine phosphate (Fig. S1). About 40% of the weight was rapidly lost up to *ca.* 270 °C, and then gradually lost. Because the decomposition temperature of guanidine phosphate is 246 °C, the decomposition of guanidine phosphate should not be the reason for the weight loss of the samples with added guanidine phosphate. These experimental results, therefore, suggest that the guanidine phosphate affected the carbonization process of the starch.

In the case of cellulose, pyrolytic degradation preferentially involves the scission of the C–O bond in the molecule because the strength of the C–O bond is lower than that of the C–C bond. This bond-breaking reaction could occur either within the ring or at the glycosidic linkage between the individual monomer units. In the first case, the molecular structure could break into CO, CO_2, H_2O, and carbonaceous char as the main products. This dehydration
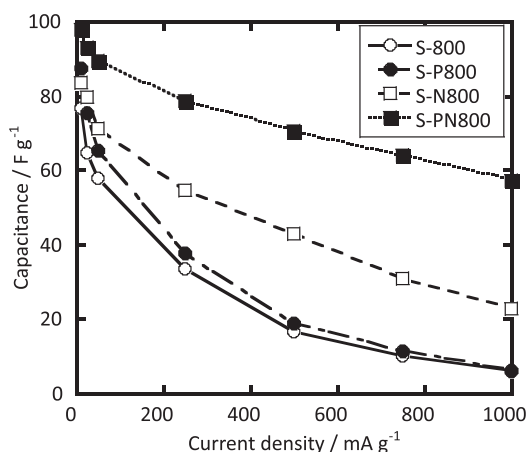

Fig. 3. The current density dependence of the capacitance values of the samples.

\reaction is favorable at low pyrolysis temperature. In the second case, the reaction could lead mainly to the formation of levoglucosan. This depolymerization reaction is favorable at high pyrolysis temperature. The main exothermic process in the combustion of cellulose is oxidation of CO to CO_2. The formation of carbon rich char should reduce the amount of the carbon oxidized to CO_2 as compared with decomposition via depolymerization process because levoglucosan could be completely oxidized in CO_2. It is known that the effect of phosphoric compounds as flame retardant for cellulose is the reduction of the pyrolysis temperature of cellulose, resulting in the enhancement of the dehydration pathway of decomposition. It is known that the flame retardant efficiency of phosphorous compound increases in the presence of guanidine. The products derived from the phosphorous–nitrogen compounds may contain the P–NH_2 groups that are presumably better dehydration catalysts than P–OH compound, which could be produced from phosphoric compound. The reason for the decrement of the starting temperature of the weight loss by the addition of guanidine phosphate in this study should be explained as above because starch has similar molecular structure to cellulose.

The amount for the added guanidine phosphate dependence of the temperature at −30% of the weight loss is shown in Fig. 4b. The temperature at −30% of the weight loss for starch was 291.0 °C. As for the sample added guanidine phosphate at 4.8 wt. %, the temperature at −30% of the weight loss was 261.7 °C. The suppression should be related to the flame retardant effect of guanidine phosphate for starch. The temperature at −30% of the weight loss slightly increased with increasing the amount of the added guanidine phosphate. The excessive addition was ineffective for decreasing the suppression of the weight loss temperature. The weight losses at 1000 °C are shown in Fig. 4c. The weight loss for starch at 1000 °C was 99.5%. The weight loss value decreased with the addition of guanidine phosphate. The weight loss decrease could be related to the flame-retardant effect of guanidine phosphate for starch. However, in the case of the excessive amount of the added guanidine phosphate, the value of the weight loss did not decrease with increasing the amount of added guanidine phosphate. Some of research works for the flame retardant of cellulose reported that the increment of the weight of the residue by the addition of the flame retardant of phosphorous-nitrogen compounds [13,14] although the final temperature was 500 °C, which was much lower than that of this study. Excessive guanidine phosphate should decompose at high temperature without acting as a flame retardant.

The DTA graphs of the samples are shown in Fig. 5a. In the case of starch, two endothermic peaks appeared at *ca.* 290 °C and *ca.* 320 °C, and there was no exothermic peak. On the other hand, for the samples with added guanidine phosphate, there was an exothermic peak at *ca.* 270 °C. These results suggest that the added guanidine phosphate reacted with the starch. The amount of the added guanidine phosphate dependence of the exothermic peak temperature is shown in Fig. 5b. The peak temperature increased with increasing the amount of the added guanidine phosphate. The temperatures of the exothermic peaks correspond to that of the sharp drop in the weight loss. Therefore, the chemical reaction of guanidine phosphate with starch might be the reason for the exothermic peak and the weight loss. Gao et al. reported the TG-DTA data of the wood treated with guanidine compound in air [16,17]. These data indicated that there were no endothermic peaks in the DTA graph of all the samples. The reason for the difference between the reported results and the data of this study should be the atmosphere of the TG-DTA measurements, that is, the reported data were measured in air while the data in this study were measured in nitrogen flow.
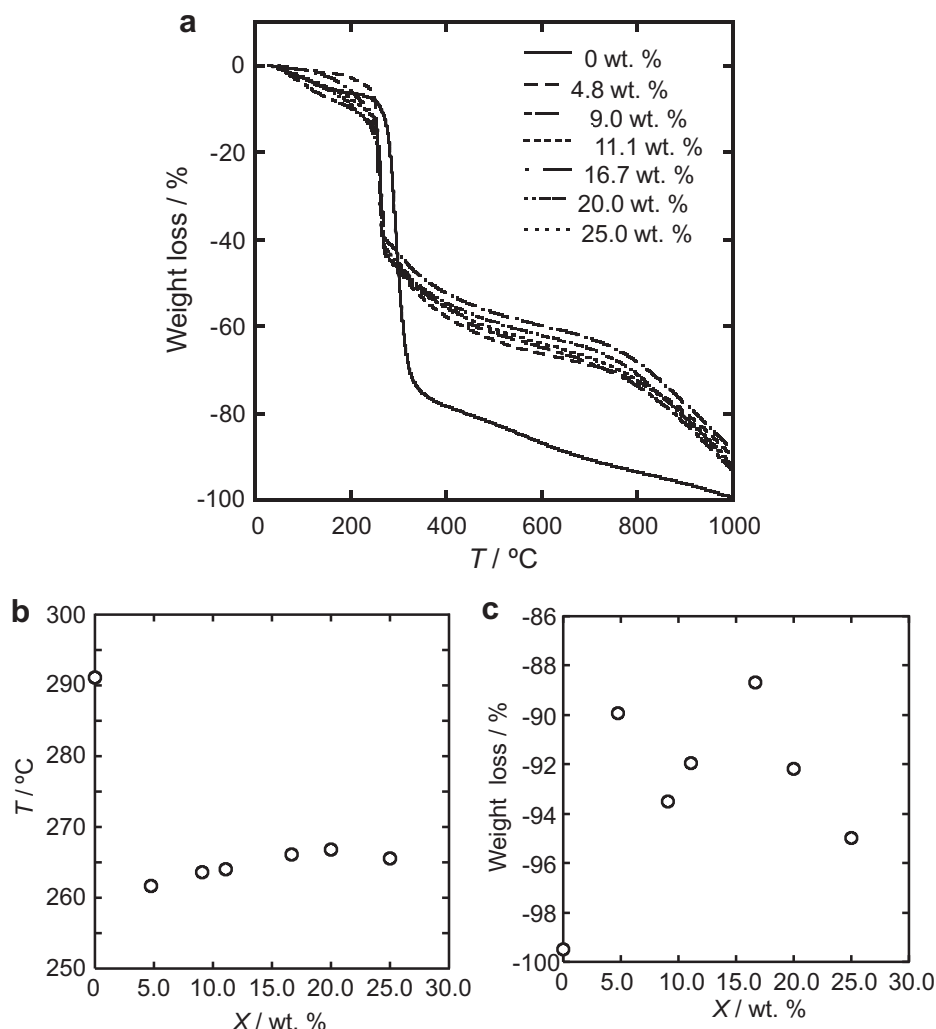
Fig. 4. The experimental results of TG measurements. (a) Temperature dependence of weight loss (b) the amount for the added guanidine phosphate dependence of the temperature at a −30% weight loss (c) the weight losses at 1000 °C.

We considered from the TG data and DTA data that guanidine phosphate should react with the starch during the heating process. Therefore, the addition of guanidine phosphate should affect the chemical condition of the sample.

3.3. Presumed reasons for the improved capacitance value

The experimental results for the measurements of the CHN corder are listed in Table 1. There were N atoms in the samples with the added guanidine phosphate. The CHN corder cannot detect phosphorus. However, the XPS data from our previous paper indicated that there are P atoms in the samples with the added guanidine phosphate. We postulate from the experimental results of Section 3.1 and Section 3.2 that N and/or P, which are derived from the guanidine phosphate, were related to the improved capacitance value.

It is currently known that phosphoric acid acts as the activator for enhancing the surface area of activated carbon [11]. In principle, a high surface area should result in a high capacitance value for the electrical double layer capacitor. Therefore, a few studies were performed involving treatment with the phosphorus compound [7,10,11]. For the sample in this study, we presumed that the effect of P was enhancement of the surface area.

Some research studies reported that some of the N-containing carbon materials have a high capacitance value [1–3]. Moreover, some papers proposed the effect of N in the material as follows [8]: Improvement of wettability against water solution; Suppression of electrical resistance; Change in electrical double layer capacitance per unit area; and appearance of pseudo capacitance.

Therefore, the possible reasons for the enhanced capacitance value of the sample mixed with guanidine phosphate are as follows:

1. Enhancement of surface area
2. Improvement of wettability against water solution
3. Suppression of electrical resistance
4. Change in electrical double layer capacitance per unit area
5. Appearance of pseudo capacitance

We can think from the principle of electrical double layer capacitor that larger surface area can be one of the reasons for the larger capacitance value if the surface condition is equal. If the wettability against the electrolyte is improved, the effective surface area which contacts with the electrolyte increases, resulting in the enhancement of the capacitance value. Smaller electrical resistance should be smaller internal resistance, resulting in the enhancement of the capacitance value. If the electrical capacitance value per unit
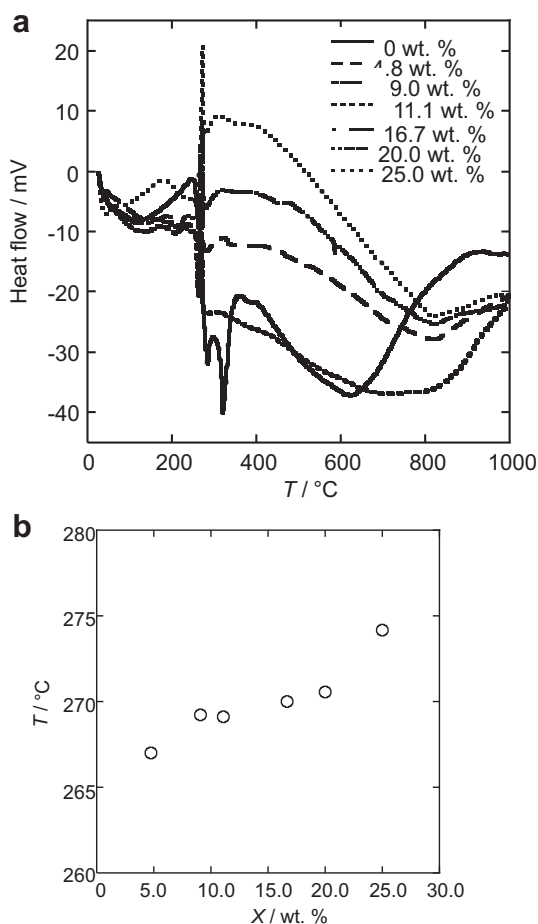
Fig. 6. The surface areas of the samples.

Fig. 5. The experimental results of DTA measurements. (a) Temperature dependence of heat flow (b) the amount of the added guanidine phosphate dependence of the exothermic peak temperature.

area increases, the capacitance value increases if the surface area is equal. If pseudo capacitance is added, the capacitance value can increase.

In this study, based on this presumption, various experiments were performed in order to investigate the reason for the improved capacitance value.

3.3.1. Surface area

As references, the sample with added guanidine carbonate or phosphoric acid was used for the following experiments. The weight ratio of the additive (guanidine carbonate or guanidine phosphate) to starch was 1:20, that is, 4.8 wt.%. In the case of phosphoric acid, the mole number of P in the added phosphoric acid water solution was the same as that in the sample with the added guanidine phosphate. The surface areas of the samples are shown in Fig. 6. As for the samples before washing with hot water, the samples except for S-PN800 had a lower surface area than S-
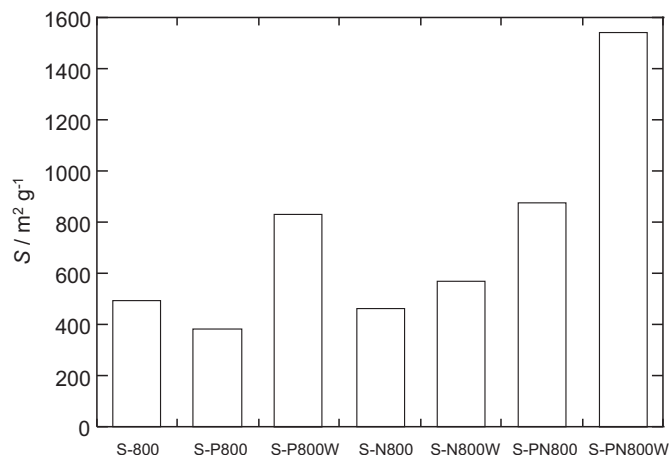
800. However, surface areas of the samples increased after the washing process, and the values were higher than that for S-800. The reason for the change in the surface area after the washing with hot water should be the removal of any impurity which can dissolve in hot water. When the additive contained P in the structure, such as phosphoric acid and guanidine phosphate, the surface areas significantly increased. The reason for the large changes in the surface area could be the activator action of P because phosphoric acid is known to be a popular activator. Therefore, with the addition of a P-containing agent, such as phosphoric acid and guanidine phosphate, the enhancement of the surface area should be one of the factors for the increased capacitance value.

3.3.2. Wettability against water solution

The contact angle was measured in order to evaluate the wettability of the sample sheets against water. The contact angles against water for the samples are listed in Table 2. The contact angles of all the samples were similar values, and the values were high. Moreover, the values of the contact angle were almost independent of the contact time with water drop. That is, the wettability of the samples was not good. The experimental results indicated that the wettability did not depend on the addition of the reagents. Therefore, the improvement of the wettability is not the reason for the increased capacitance value.

3.3.3. Suppression of electrical resistance

The electrical resistance of the samples estimated from the results of the Nyquist plots for the samples are shown in Fig. 7. The electrical resistance decreased with the addition of the N-containing reagents. Some papers reported that the N-doping decreased the intrinsic resistance of carbon when the ratio of N in the carbon sample was low (N/C atomic ratio: 0.025 or 0.075) [8,20]. When the ratio of N in the carbon sample was high such as ca.30 at.%, the electrical resistivity increased because the presence of C≡N bonds induced many ruptures in the graphitic network [21,22]. In the case of this study, the electrical resistances should be

Table 1
The experimental results of CHN corder.

The amount of guanidine phosphate/wt.%	C/wt.%	H/wt.%	N/wt.%	Others/wt.%
0	78.24	1.42	–	20.34
4.8	75.33	1.84	3.15	19.68
9.0	66.37	1.9	2.77	28.96
16.7	64.82	1.77	3.55	29.86
25.0	63.13	1.77	3.57	31.53

Table 2
The contact angles against distilled water of the sheet samples.

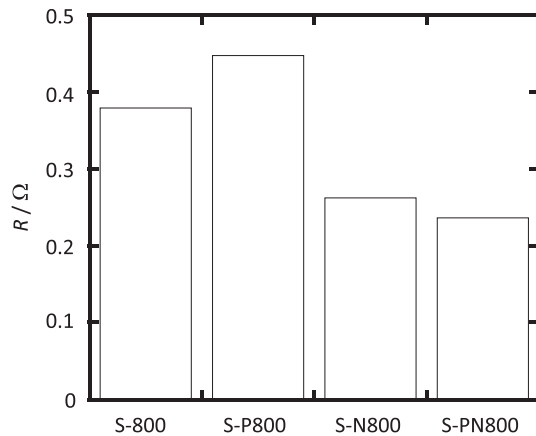| Sample	0 s	180 s
S-800	128.9°	126.5°
S-P800	123.9°	121.8°
S-N800	126.7°	122.8°
S-PN800	120.5°	118.0°

Fig. 7. The electrical resistance of the samples estimated from the results of the Nyquist plots for the samples.

suppressed because the percentage of N in the sample was low (as shown in Table 4). As for S-N800 and S-PN800, the suppression of electrical resistance should be one of the reasons for the change in the capacitance value.

3.3.4. Electrical double layer capacitance and pseudo capacitance

In order to separate the electrical double layer capacitance from pseudo capacitance, the simple method reported by Ziyin [23] was applied to the figures of the CV data although the method was rather rough. That is, the perfect rectangular area in the CV curve was ascribed to the electrical double layer capacitance and the other area was ascribed to the pseudo capacitance. The capacitance value per unit surface area was calculated from the estimated capacitance values for each component and the specific surface area after washing with hot water. The calculated results are shown in Fig. 8a. The estimated electrical capacitance value per unit surface area of S-P800 was almost the same as that of S-800. These results could indicate that the surface property for the electrical double layer capacitance did not change by the addition of phosphoric acid. On the other hand, in the case of S-N800, the estimated electrical capacitance value per unit surface area was much higher than that of S-800. The existence of N in the compound should enhance the electrical double layer capacitance per unit surface area because some of the N-containing carbon materials were reported to have a high capacitance value per surface area [24]. The calculated electrical double layer capacitance value per unit surface area for S-PN800 was similar to that of S-800. This could mean that the reason for the high capacitance value of S-PN800 was not the enhancement of the electrical double layer capacitance per unit surface area.

The calculated values for the pseudo capacitance are shown in Fig. 8b. All the samples mixed with the additives had higher pseudo capacitance values than S-800 although the absolute values were smaller than those of the electrical double layer capacitance. Therefore, in the case of S-N800, the enhancement of the capacitance value should be caused by both the change in the electric double layer capacitance and the change in the pseudo capacitance, and for S-P800 and S-PN800, the enhancement of the capacitance value should be caused by the change in the pseudo capacitance. As for S-PN800, both the value of the electrical double layer

Table 3
The N conditions estimated from the XPS data.

	N in pyridine structure	Quaternary N	N in nitric oxide
S-N800	36.1%	50.7%	13.1%
S-PN800	28.6%	52.5%	18.8%

Table 4
The calculated percentages of the elements.

Sample	C/at.%	O/at.%	N/at.%	P/at.%
S-800	88.5	11.5	0	0
S-P800	94.63	3.88	0.99	0.49
S-N800	93.4	4.98	3.62	0
S-PN800	87.42	7.64	3.89	1.05

capacitance per surface area and the value of the pseudo capacitance per surface area were not the highest values. Therefore, a high surface area should be the main reason for the high capacitance value of S-PN800.

The XPS measurements were performed in order to evaluate the condition of N in the samples as shown in Fig. S2. The estimated values based on ref. [8] are listed in Table 3. Moreover, the percentages of the elements in the samples were measured by XPS. The calculated percentages are listed in Table 4. The percentage of N for S-N800 was similar to that for S-PN800, that is, 3−4%. It is reported that the N in the pyridine structure contributed to the enhancement of the pseudo capacitance [9]. The quaternary N also may contribute to the increase in the pseudo capacitance because the N atom should have a positive electric charge. The higher percentage of the sum of the N in the pyridine structure and the
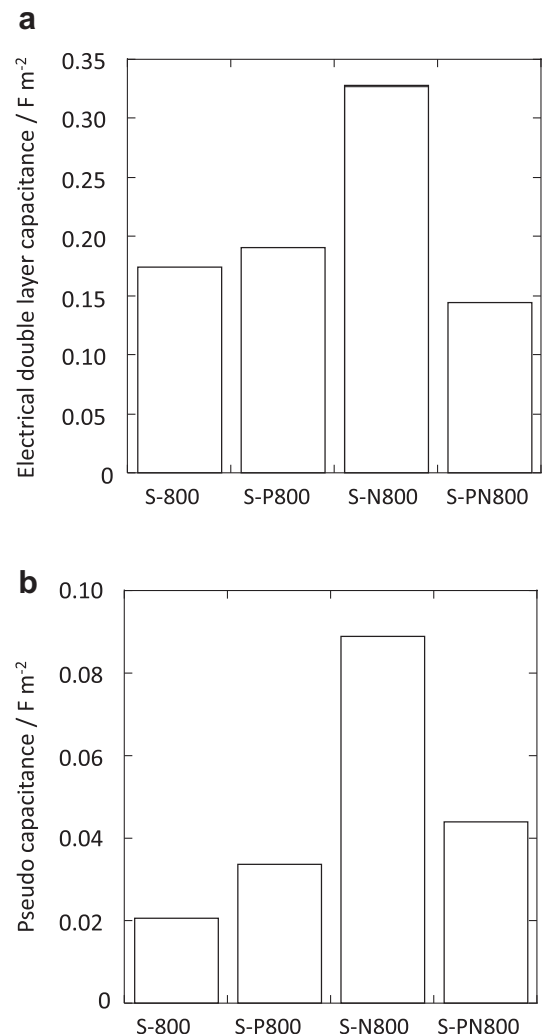

Fig. 8. The capacitance value per unit surface area. (a) Electrical double layer capacitance (b) pseudo capacitance.

quaternary N for S-N800 should be related to the higher pseudo capacitance.

3.4. Effect of the addition of guanidine phosphate

The effects of the addition of guanidine phosphate are concluded as follows:

1. Enhancement of the surface area is the main reason for the enhancement of the capacitance value.
2. There is no improvement in the wettability against water solution.
3. Suppression of the electrical resistance is one of the reasons for the improvement in the capacitance value.
4. The change in the electrical double layer capacitance per surface area is not reason for the change in the capacitance value.
5. Appearance of the pseudo capacitance is one of the reasons for the improved capacitance value.

4. Conclusions

The characterizations of the carbon material derived from the starch mixed with guanidine phosphate were investigated in detail. The reasons for the enhanced capacitance value are summarized. The main reason for the enhancement should be the change in the surface area, which could be caused by the effect of P. Suppression of the electrical resistance and the appearance of the pseudo capacitance, which could be caused by the N in the pyridine structure and the quaternary N, are also reasons for the enhanced capacitance value.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2012.11.042.

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